

THE REACTIONS OF THE TOSYLHYDRAZONE

FROM α -CHLOROISOBUTYRALDEHYDE

A THESIS

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BY

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
ABSTRACT	iii
INTRODUCTION	1
RESULTS AND DISCUSSION	11
EXPERIMENTAL	26
REFERENCES	33

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ABSTRACT

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The Reactions of the Tosylhydrazone from α -Chloroisobutyraldehyde

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Master of Science degree conferred May 1972

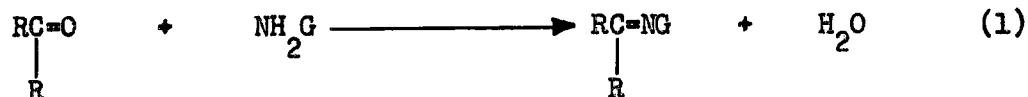
Thesis dated May 1972

Para-toluenesulfonylazo-2-methylpropene has been prepared from the tosylhydrazone of the corresponding α -chloroaldehyde. The p-tosylazoene obtained is a yellow compound that decomposes at room temperature within minutes with the evolution of nitrogen. Because of the instability of the azoene, its structure has been assigned on the basis of spectroscopic evidence.

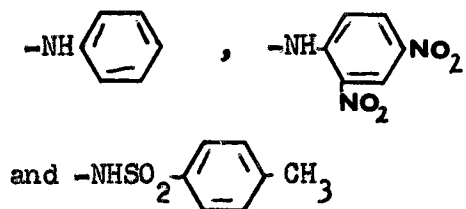
The course of the decomposition of the tosylazoene has been followed at 10° in aprotic solvents by nuclear magnetic resonance spectroscopy. Evidence that the reaction proceeds in part through the formation of the diazo compound was obtained from the isolation of 2-methyl-p-toluenesulfonylhydrazone which is formed from the 1,4-addition of p-toluenesulfinic acid to the undecomposed 1-p-toluenesulfonylazo-2-methylpropene.

INTRODUCTION

The condensation reaction of aldehydes and ketones with ammonia derivatives is a well known reaction. This general reaction is illustrated in equation (1).



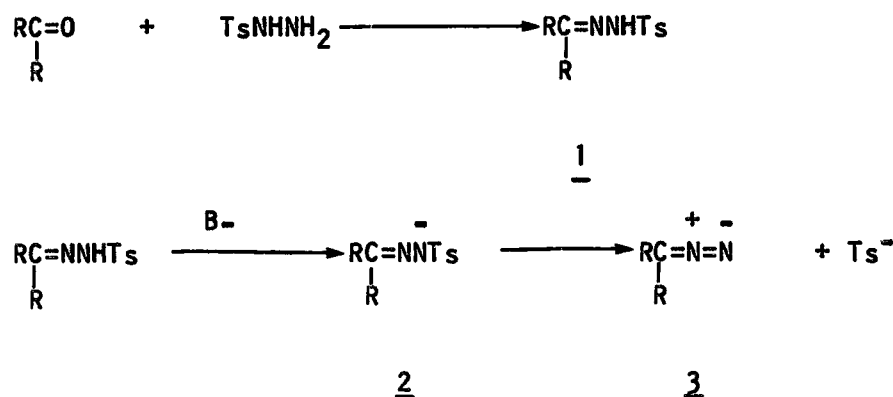
where G = -OH, -NH₂, -NHCH₃, -NHCONH₂,



The particular kind of derivative studied in this research project is the tosylhydrazone formed when an aldehyde or ketone reacts with p-toluenesulfonylhydrazide. In the following pages some of the reactions that tosylhydrazones undergo will be discussed briefly.

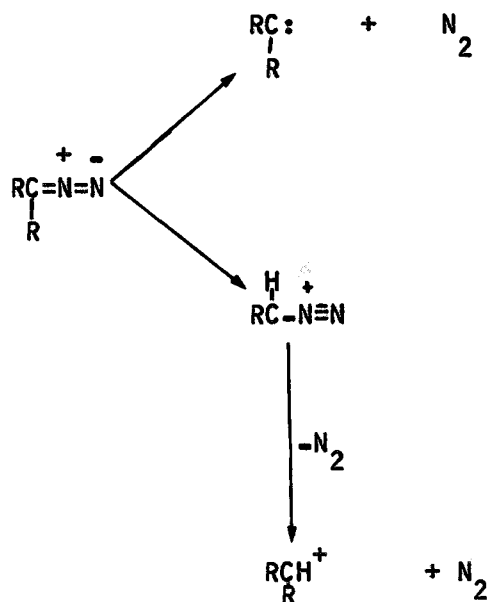
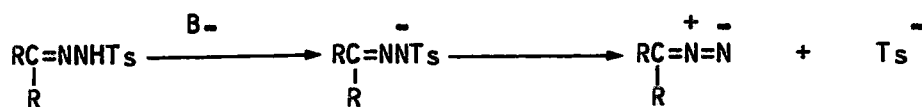
Bamford and Stevens¹ first studied the reaction of a tosylhydrazone 1 with a base. In the absence of protic solvents the tosylhydrazone 1 decomposed via the p-toluenesulfinate ion 2 to

give the diazo compound 3.

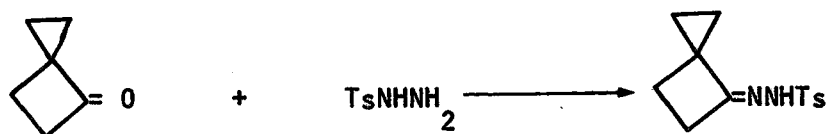
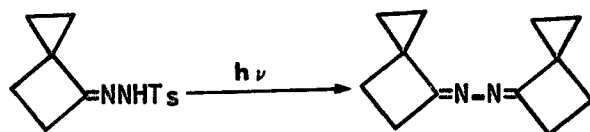


Friedman and Shechter² later showed that the basic decomposition of p-toluenesulfonylhydrazone in the Bamford-Stevens reaction may be used as a general method for the formation of carbenes since the intermediate diazo compound usually decomposes under the reaction conditions.

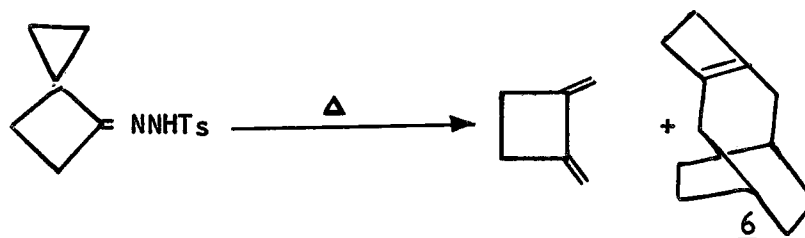
Once generated, the diazo compound 3 could undergo carbenic decomposition in aprotic solvents to give olefins by hydrogen migration and a cyclopropane by intramolecular insertion or alternatively in protic solvent, the diazo compound could also undergo proton transfer from donor solvent and cationic decomposition of the Wagner-Meerwein type involving rearrangement.³ In both cases p-toluenesulfinic acid and nitrogen are obtained. The mechanisms for these reactions are illustrated below.



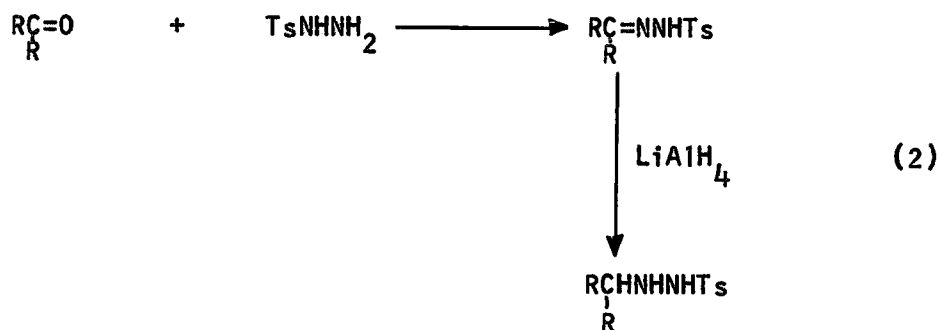
Wiberg and coworkers⁴ found that in the photolysis of the sodium salt of spiro [2.3] hexanone-4-tosylhydrazone (4) in diglyme or dimethyl sulfoxide, the azine 5 is formed.

45

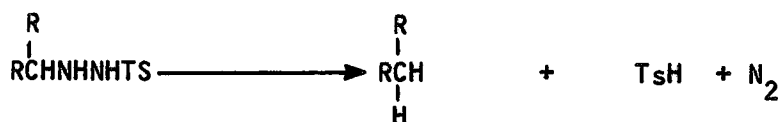
On the other hand, thermolysis of 4 gave different products one of which corresponded to the Diels-Alder adduct of $\Delta^{1,4}$ -bicyclo [2.2.0] - hexene and 1,2-dimethylenecyclobutane.⁵



The reduction of the double bond ($>C=N-$) of a tosylhydrazone forms a hydrazide⁶ (Equation 2).



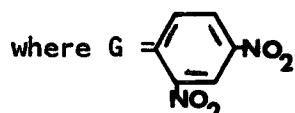
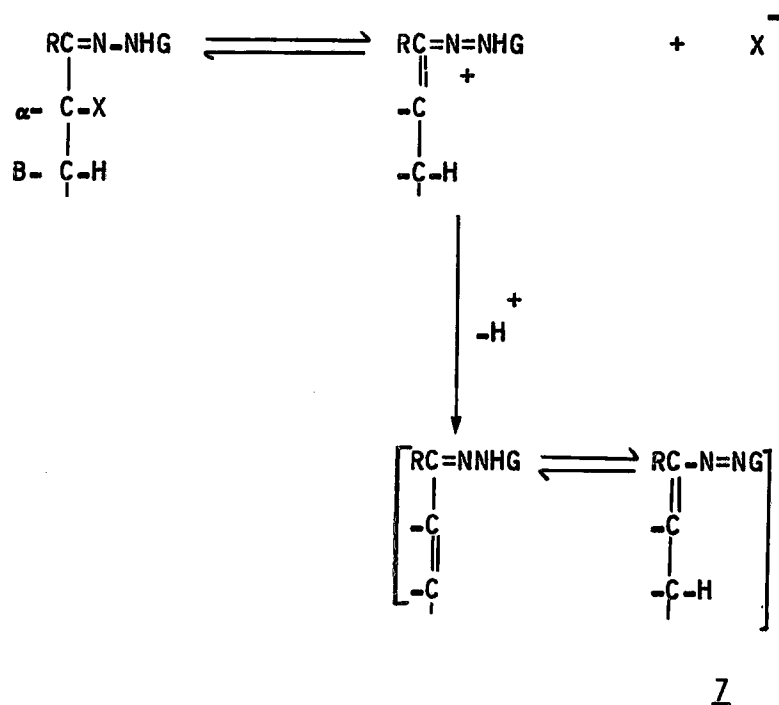
The alkyl tosylhydrazides can also undergo thermal decomposition in protic or aprotic solvents, with or without basic catalysis, to form a saturated hydrocarbon and p-toluenesulfinic acid.⁷



Our particular interest, however, lies in the reaction of hydrazones formed in which there is an α -leaving group present in the molecule.

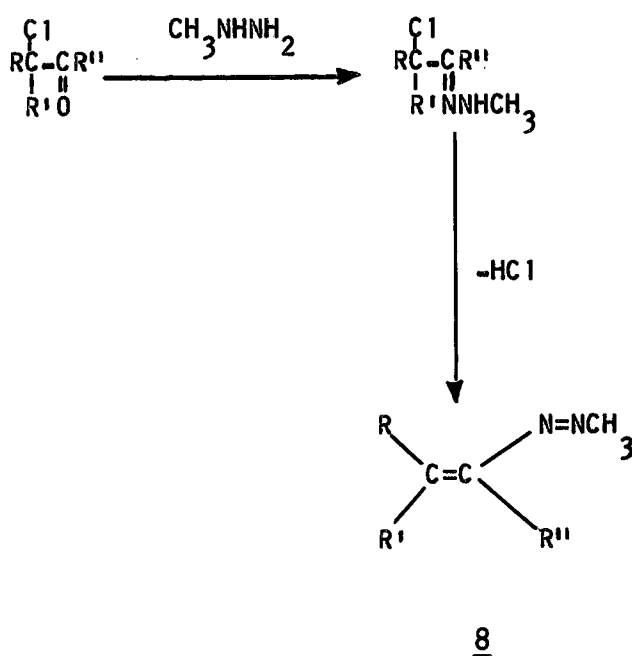
In order to provide background information and to point out the nature and scope of this particular study, a brief review of the more recent and interesting reactions of hydrazines and α -substituted carbonyl compounds will be discussed.

The reaction of the carbonyl reagent, 2,4-dinitrophenylhydrazine, on α -haloketones was reported by Kirby and Ramirez⁸ to involve the formation of an intermediate azo compound I.

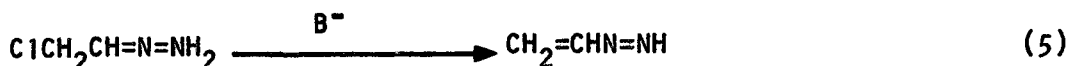
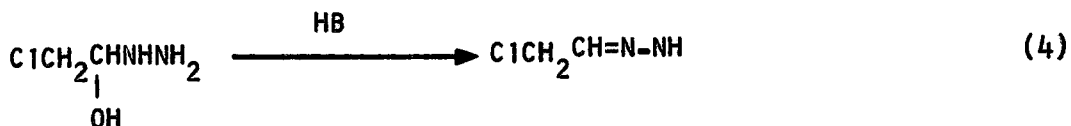


The above scheme, which does not imply classification into a fixed mechanistic category, is based essentially on earlier suggestions of Mattox and Kendall⁹ from their studies on the steroidal α -bromo-2,4-dinitrophenylhydrazones.

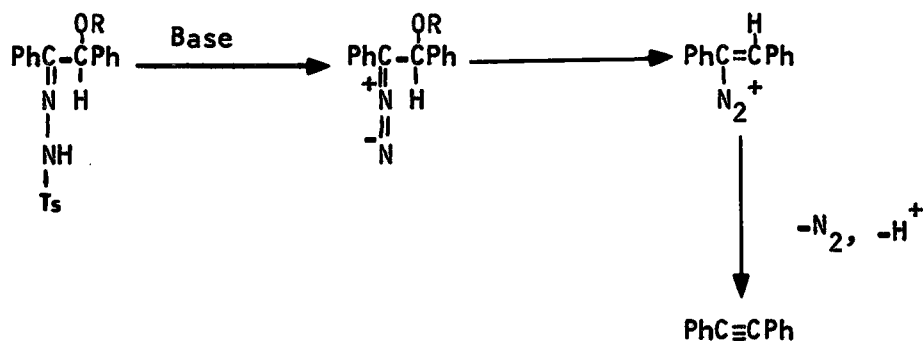
Newer evidence provided by Gillis and Hagarty¹⁰ in their successful synthesis of α,β -unsaturated azo compounds from the reaction of α -chloroaldehydes and ketones provided more insight into the mechanism for this type reaction. The mechanism indicated stepwise formation of the hydrazone from the α -substituted carbonyl followed by 1,4-dehydrohalogenation to form the diazene 8.



Similar results were obtained by Tsuiji and Kosower¹¹ when they applied the reaction to α -chloroaldehydes and hydrazine under oxygen-free conditions. Again, 1,4-dehydrohalogenation to form the unsaturated azo compound was utilized. The formation of the vinyldiazene from chloroacetaldehyde is illustrated in equations 3-5.¹¹



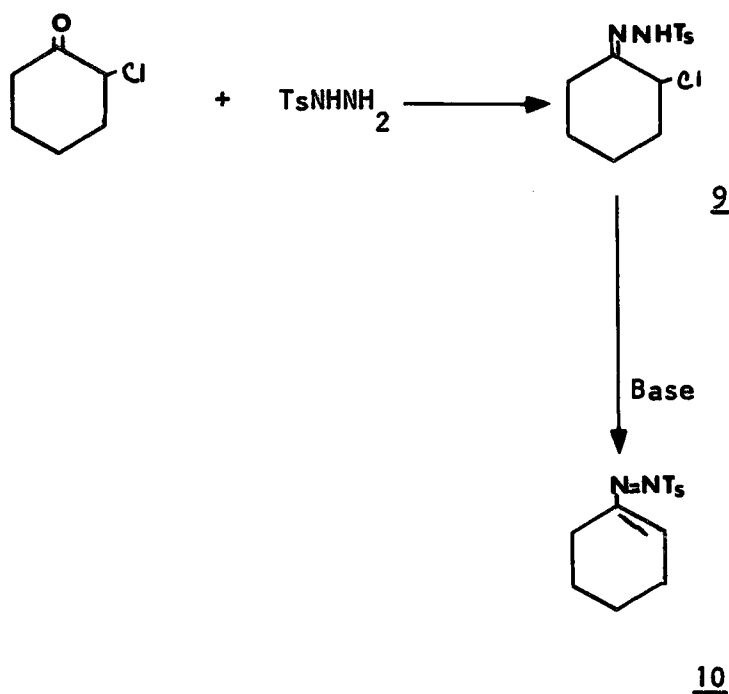
Other investigations of the reactions of α -substituted carbonyl compounds with hydrazine have been made. Iwadare and coworkers¹² have converted benzoin benzoate and benzoin acetate into their respective tosylhydrazones. The authors further report that diphenylacetylene is obtained as one of the major products in the decomposition of the azo compound. The formation of diphenylacetylene via the tosylhydrazone of benzoin acetate is illustrated below.



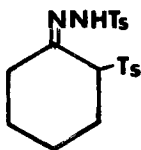
It is perhaps noteworthy that subsequent to these results, Wieland,¹³ in the study of the p-tosylazoene formed from α -sulfonyloxy groups,

and Rosini and coworkers¹⁴ independently reported that the treatment of acetoxydeoxybenzoin with tosylhydrazide also afforded diphenylacetylene. The mechanism for the formation of these compounds is consistent with 1,4-elimination by basic treatment of the tosylhydrazone which is in variance to the mechanism proposed by Iwadare and coworkers.¹²

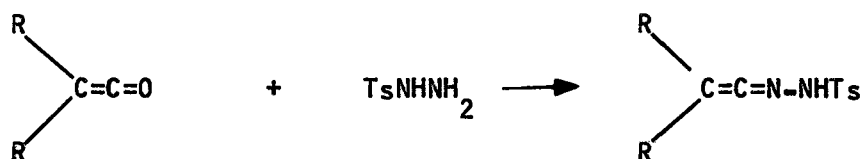
Though the chemistry of tosylhydrazones has been the subject of considerable research during the past two decades, not much work has been published on the tosylhydrazones formed from compounds with a halo group attached to the adjacent carbon. The only tosylhydrazone derivative prepared thus far from a α -halo carbonyl was prepared by Rosini, Rossi and Cagliotti¹⁵ who applied the reaction of p-toluenesulfonylhydrazide and α -chlorocyclohexanone to form the tosylhydrazone 9. Elimination of hydrogen chloride forms the tosylcyclohexene 10.



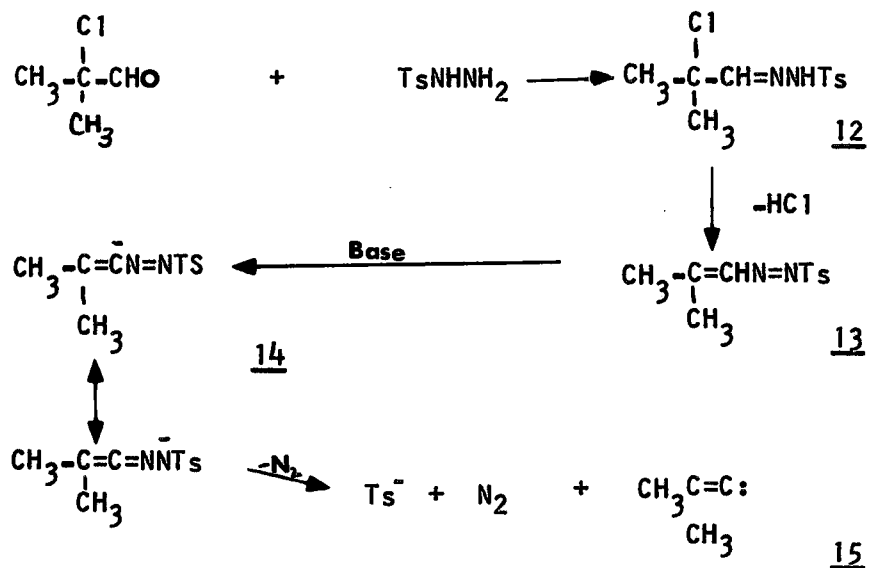
When the reaction was run in a protic solvent the following compound was isolated which they proposed was formed by 1,4-addition of sulfinic acid to the azoene 10.



This work on α -substituted hydrazones led us to consider the possibility of vinylidene formation from the p-tosylhydrazones formed from α -substituted aldehydes. It is not possible to form the tosylhydrazone required for the Bamford-Stevens reaction directly.



However, a proposed alternate method of forming the anion of the tosylhydrazone is shown in the following mechanism.

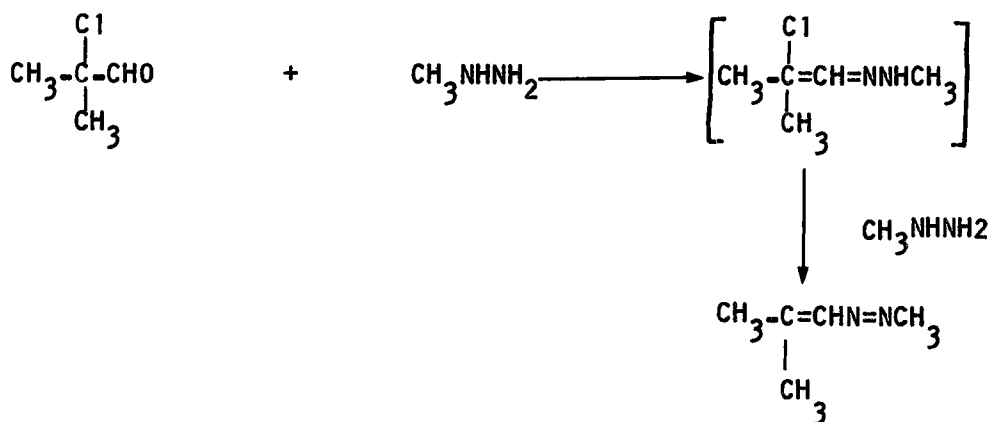


The removal of the vinyl hydrogen from 13 with a suitable base would yield the sulfone diazene anion 14. Subsequent elimination of nitrogen and the *p*-toluenesulfinate anion would form the carbene 15. All attempts to form and trap 15 in our laboratory have failed.

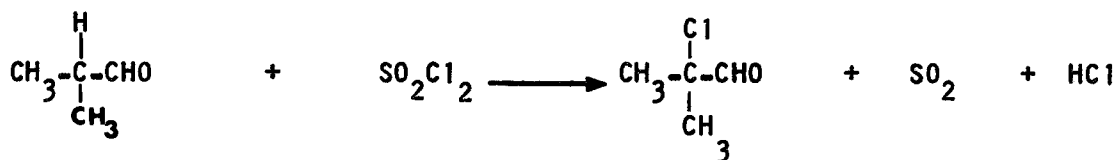
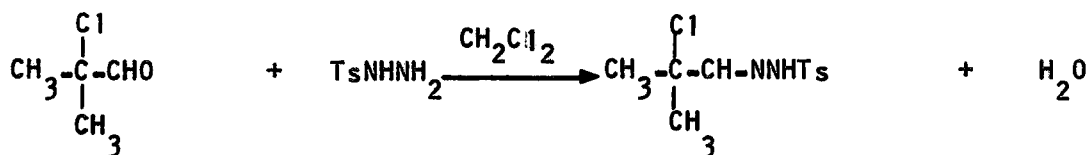
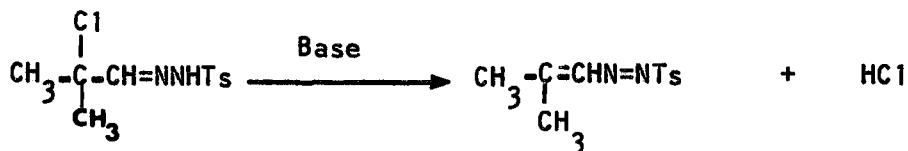
RESULTS AND DISCUSSION

The tosylhydrazones (p-toluenesulfonylhydrazones) of α -substituted carbonyls react with a base in aprotic solvents to give the corresponding α,β -unsaturated azo compound.¹⁶ This investigation reports the formation of the azo compound formed from the α -chloroisobutyraldehyde tosylhydrazone and the reaction it undergoes.

A search of the literature reveals that a hydrazone of α -chloroisobutyraldehyde has been prepared. Gillis and Hagarty¹⁰ reported the synthesis of 1-(methylazoisobutylene)-2 using two equivalents of methylhydrazine.



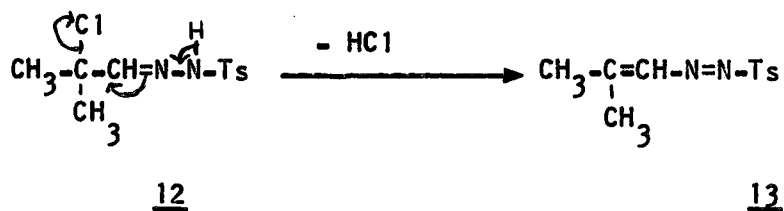
The synthesis of the corresponding tosylhydrazone outlined in the flow chart below, was accomplished in good yields and with little difficulty.

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Alpha-chloroisobutyraldehyde (11) was prepared by direct chlorination of isobutyraldehyde according to the procedure of Stevens and Gillis.¹⁷ Treatment of 11 with an equimolar equivalent of p-toluenesulfonylhydrazide in methylene chloride gave 12 in 100 percent yield. The white solid collected after evaporation of the solvent in vacuo was identified by conventional methods. The nuclear magnetic resonance spectrum showed bands at $\delta=1.76$ (6H, singlet, gem dimethyl), 2.51 (3H, singlet, p-ArCH₃), 5.41 (1H, singlet, -NH-), 7.42 (2H, doublet, p-ArH, $J=8$ Hz) and 7.86 (5H, doublet, p-ArH and >C=CH- , $J=8$ Hz) ppm. Principal infrared (ir) bands were observed at 2.95, 3.30, 6.25, 6.85, 7.21 and 7.30 μ . Further

attempts to purify 12 through recrystallization resulted in decomposition.

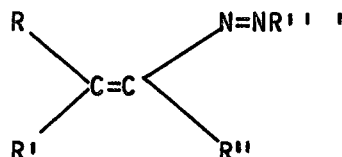
When 2-methyl-2-chloropropanal-p-toluenesulfonylhydrazone (12), dissolved in anhydrous ether, was treated with a saturated sodium bicarbonate solution, the characteristic yellow color of the unsaturated azo compound developed and 1-p-toluenesulfonylazo-2-methylpropene (13) was isolated in 100 percent yield. The mechanism for the formation of 13 is consistent with 1,4-elimination of hydrogen chloride by basic treatment (Scheme I). The resulting azoene decomposes within a few minutes at room temperature but is stable for a few hours at zero degrees.



Scheme I

The nuclear magnetic resonance spectrum of this compound at -10° showed singlets at $\delta=2.16$ (6H, gem dimethyl), 2.52 (3H, p-ArCH₃), 7.06 (1H, >C=CH-) and doublets at 7.46 (2H, p-ArH, $J=7$ Hz) and 7.74 (2H, p-ArH, $J=7$ Hz) ppm. The shift to lower field (deshielding) for the gem dimethyl protons is expected since the π -electron density for these protons increases. The concentration of the π -electron density created places both methyl groups in the deshielding area resulting in a shift of ca. 0.4 ppm downfield from internal tetramethylsilane.

Azo compounds possess, as expected, two light absorption bands in the ultraviolet-visible region, a weak absorption ($n-\pi^*$ transition) and a strong absorption ($\pi-\pi^*$ transition). Gillis and Hagarty¹⁰ have completed ultraviolet studies on α,β -unsaturated aliphatic azo compounds and have observed that for



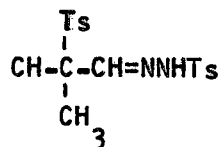
the uv maximum when R'' is an N-alkyl substituent is $\lambda_{252} \text{ m}\mu$ ($\epsilon 7,490$) and for N-phenyl substituents, $\lambda = 317 \text{ m}\mu$.

Our investigation of the uv absorption of 13 showed three bands, (cyclohexane)
 $\lambda_{\text{max}} \quad 227 \text{ m}\mu (\epsilon 6800), 277 \text{ m}\mu (\epsilon 14,545) \text{ and } 420 \text{ m}\mu$
 ($\epsilon 10$). The band at $227 \text{ m}\mu$, due to $\pi-\pi^*$ transition (K-band), was assigned to the substituted aromatic system. An ultraviolet spectrum taken of 12 also shows one band recorded at $226 \text{ m}\mu$. Because the $>\text{C}=\text{N}$ - chromophore is not attached directly to the conjugated system in 12, there is no change in the position of absorption. In addition the band at $\lambda_{\text{max}} 420 \text{ m}\mu$ disappeared after a few hours with change in color of the sample solution.

Low temperature nmr studies of 13 have been done in carbon tetrachloride and chloroform-d at -10° , -5° , 5° and 10° . At -10° the

absorption due to the geminal methyl protons appears as a singlet, $\delta=2.16$ ppm.

The decomposition of 1-p-toluenesulfonylazo-2-methyl-propene (13) and its rearrangement was followed by scanning on the nmr at 15 min time intervals at 10°. Although no measurements of the rate of decomposition have been carried out, the disappearance of the peak at $\delta=2.16$ ppm and the appearance of peaks at $\delta=1.79$ and 1.08 ppm were followed. The peak at $\delta=1.79$ is consistent with formation of 2-methyl-2-tosylpropane-1-toluenesulfonylhydrazone (16).



16

At room temperature, the decomposition of 13 in carbon tetrachloride resulted in the evolution of nitrogen and the disappearance of the yellow color of the solution. The mixtures obtained by evaporation of the solvent in vacuo were separated by column chromatography on neutral alumina. The same results were obtained if 13 was allowed to stand in chloroform. Gas evolution was determined to be ca. 50 percent yield by volume of the available amount of nitrogen gas. Tests for unsaturated products in the evolved gas were negative.

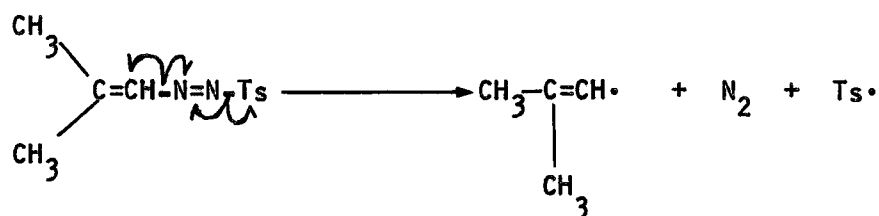
The advantage of using carbon tetrachloride as a solvent during the decomposition of 13 is that a white solid, determined to be 16, is isolated directly which can be further purified by column chromatography. The yield of product in both cases were approximately the same, eleven and twelve percent, respectively.

Because of the instability of the azo compound 13 the mechanism of its decomposition has been investigated. Azo compounds are known to decompose thermally to yield free radicals and nitrogen.^{18,19} The rate of the decomposition reaction is markedly influenced by the stabilities of the radicals produced. The lability of aliphatic azo compounds depends on the nature of the substitution, "mixed" alkyl-aryl azo compounds being more stable. However, when α -substitution capable of stabilizing the resulting free radicals are introduced, homolytic fission occurs more readily. The azo compound decomposes readily in the temperature range of 60° to 150° (See table 1) and its decomposition is not induced by solvent derived radicals.

Table 1. Activation Energies for Thermal Decomposition of Azo Compounds.²⁰

Azo Compound	Radicals Produced	Solvent	ΔE^*
$\text{CH}_3\text{N}=\text{NCH}_3$	$\text{CH}_3\cdot$	Gas	50.2
$(\text{CH}_3)_2\text{CHN}=\text{NCH}(\text{CH}_3)_2$	$(\text{CH}_3)_2\text{CH}\cdot$	Gas	40.9
$(\text{CH}_3)_3\text{CN}=\text{NC}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}\cdot$	Gas	43
$(\text{C}_6\text{H}_5)_2\text{CHN}=\text{NCH}(\text{C}_6\text{H}_5)_2$	$(\text{C}_6\text{H}_5)_2\text{CH}\cdot$	Toluene	26.6
$(\text{CH}_3)_2-\underset{\text{CN}}{\text{CN}}=\underset{\text{CN}}{\text{NC}}-(\text{CH}_3)_2$	$(\text{CH}_3)_2\underset{\text{CN}}{\text{C}}\cdot$	Toluene	31.3

The thermal decomposition of the azo compounds to free radicals (indicated in Table 1), coupled with the relative instability of 13, led us to consider the possibility of 13 decomposing via a free radical mechanism. The mechanism for such a reaction is illustrated below in Scheme II.

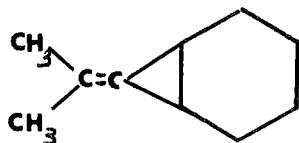


Scheme II

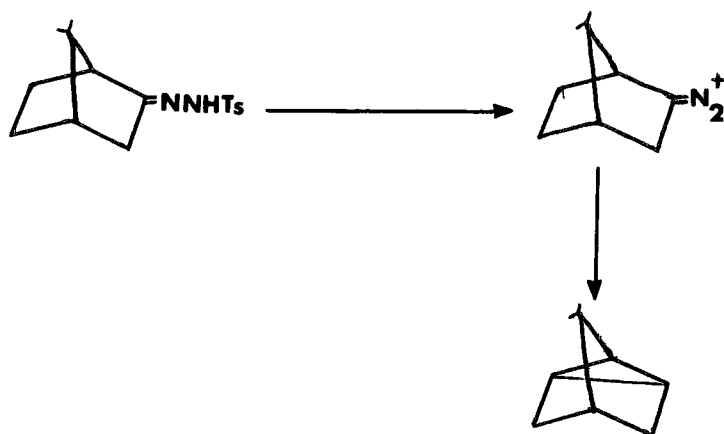
However, no signals were recorded when an electron spin resonance spectrum was taken of the decomposing sample in chloroform.

Since there is evidence that the decomposition of azo compounds can proceed through the formation of carbenes,^{3,21} this reaction was attempted in our laboratory. The *p*-toluenesulfonylazoene (13) was treated respectively with sodium methoxide, sodium hydride and potassium tertiary-butoxide in cyclohexene. In each case a bright yellow color developed initially, but rapidly faded. Gas liquid chromatographic analysis indicated no hydrocarbon at the approximate retention

time of the adduct shown below.

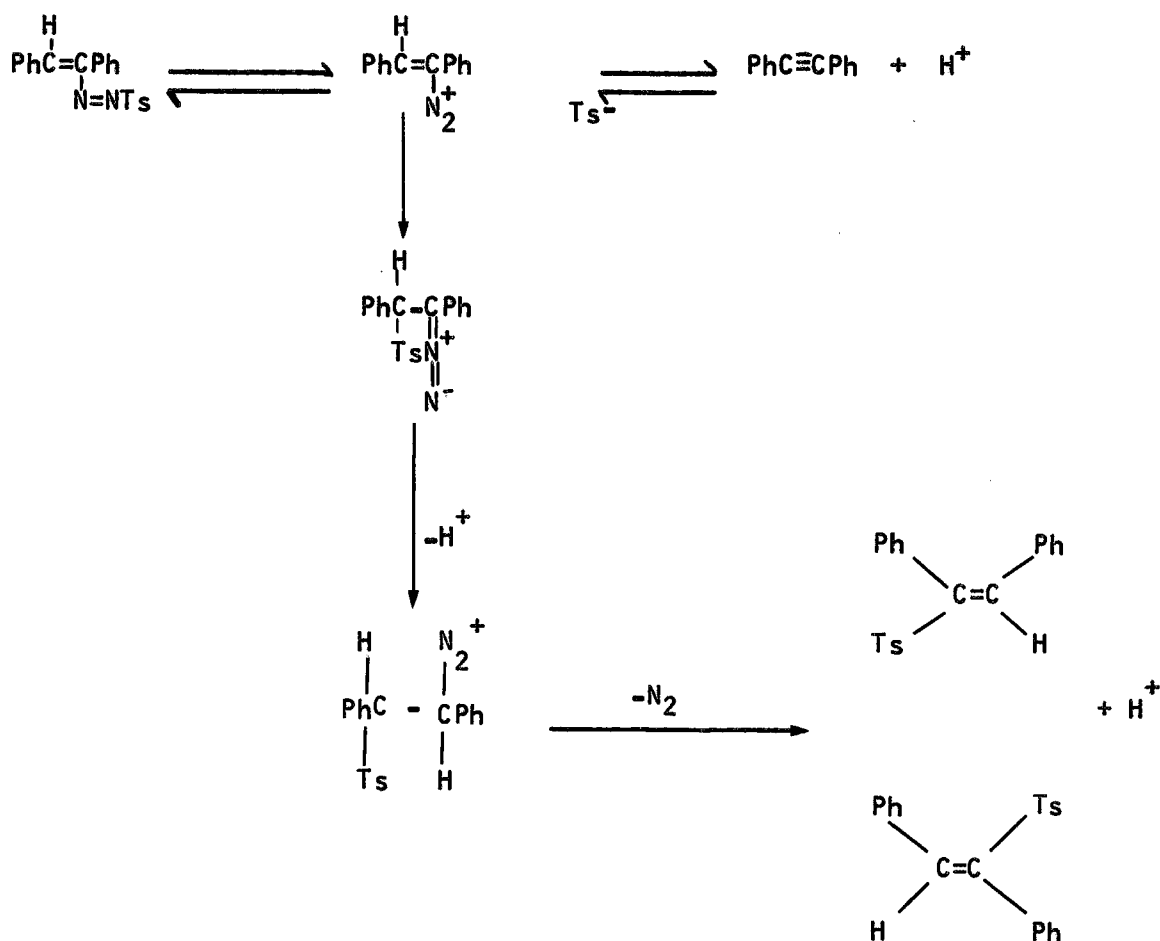


In the study of the decomposition of the camphor tosylhydrazone Powell and Whiting²² have indicated that the two steps, loss of nitrogen and rearrangement to form an olefin, are simultaneous so that no free carbene is involved.

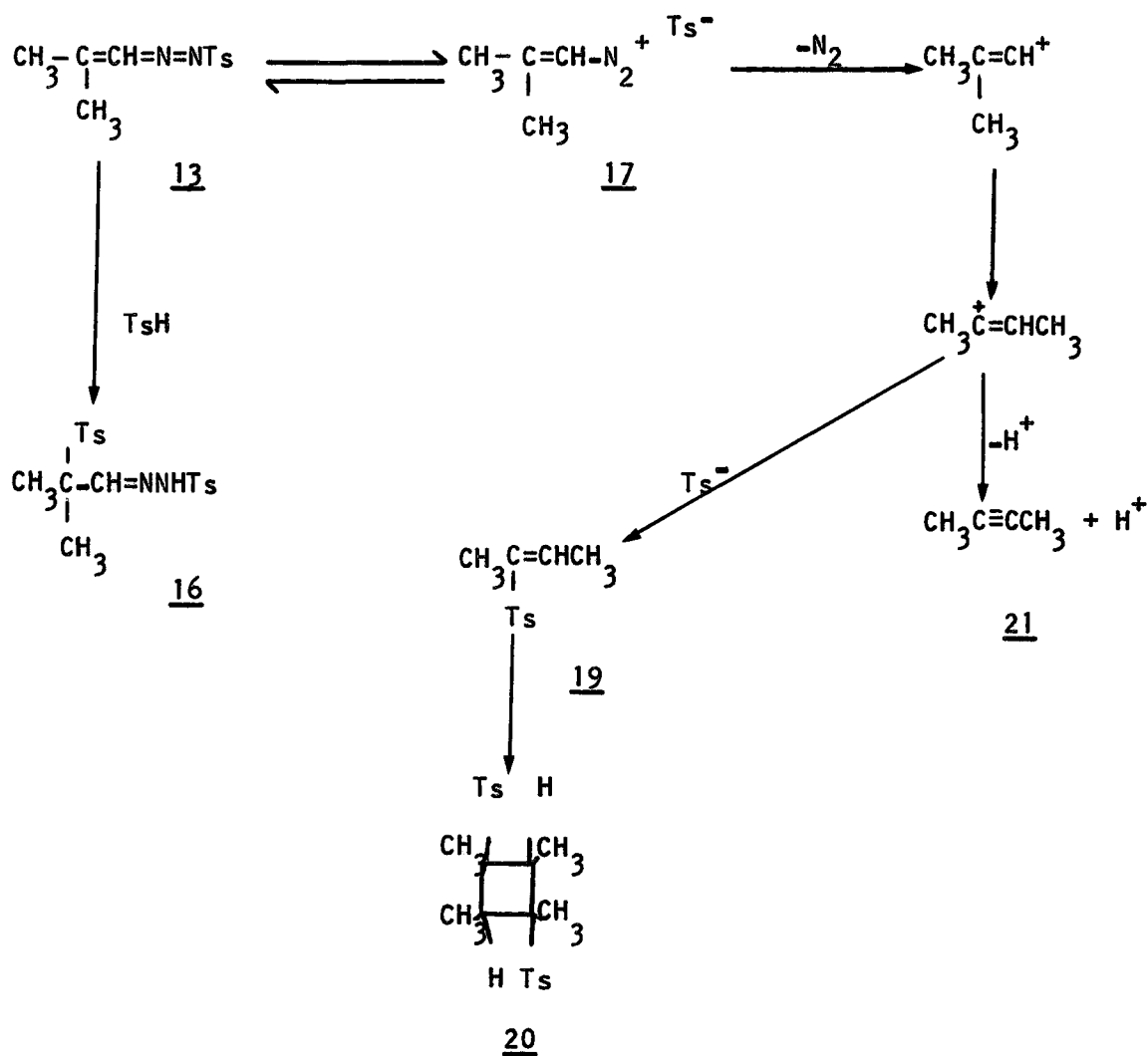


Therefore, although the mechanism involving a free carbene can be ruled out in our case, a mechanism involving simultaneous elimination of nitrogen and insertion into a C-H bond is still possible.

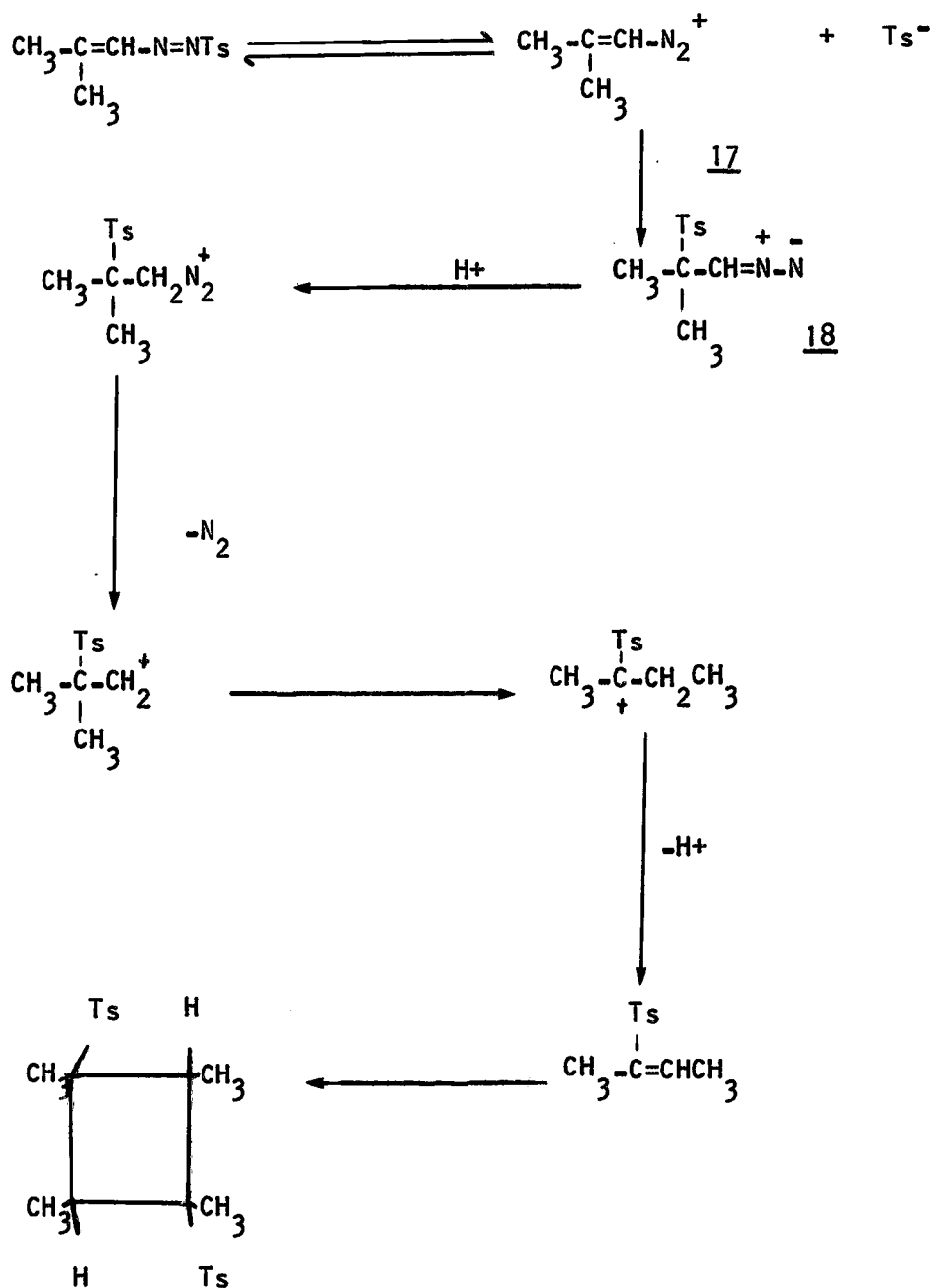
While the work in our laboratory was in progress Rosini and coworkers¹⁴ reported a detailed investigation of the decomposition of two p-toluenesulfonylazoalkanes: 2-p-toluenesulfonylazo-1,3-diphenylpropene and p-toluenesulfonylazo-1,3-diphenylstilbene. The mechanism they postulated to account for the formation of diphenylacetylene and p-toluenesulfonylstilbene from 2-p-toluenesulfonylazo-1,3-diphenylpropene is illustrated in the flow chart below.



The theoretical implications from Rosini's¹⁴ and Cagliotti's¹⁵ investigations have been extensively examined by the author. The results in this paper and the isolation and identification of compound 16 are in good agreement with the results of Cagliotti and Rosini. If the decomposition of 13 follows a pathway similar to that proposed by Rosini¹⁴ the decomposition can be outlined as depicted in Scheme III, pathway 1 or 2.



SCHEME III, Pathway 1



SCHEME III, PATHWAY 2

We suggest that the formation of 16 takes place as follows: a part of the p-toluenesulfonylazoene (13) dissociates into the diazonium-p-toluenesulfinate (15) which then loses nitrogen and p-toluenesulfinic acid. The p-toluenesulfinic acid adds by a 1,4-mechanism to the azoenic system of undecomposed 13 leading to the formation of 2-methyl-2-tosylpropanal-p-toluenesulfonylhydrazone (16). Product 16 was isolated as a white solid mp 137°. In the nmr spectrum, 16 showed bands at $\delta=1.50$ (6H, singlet, gem dimethyl), 2.51 (6H, singlet, p-ArCH₃) and 7.2-7.8 (9H, multiplet, p-ArH and -CH=)ppm. Principal ir bands were observed at 2.95 (w), 6.3 (m), 7.22 (m) and 7.32 (m) μ .

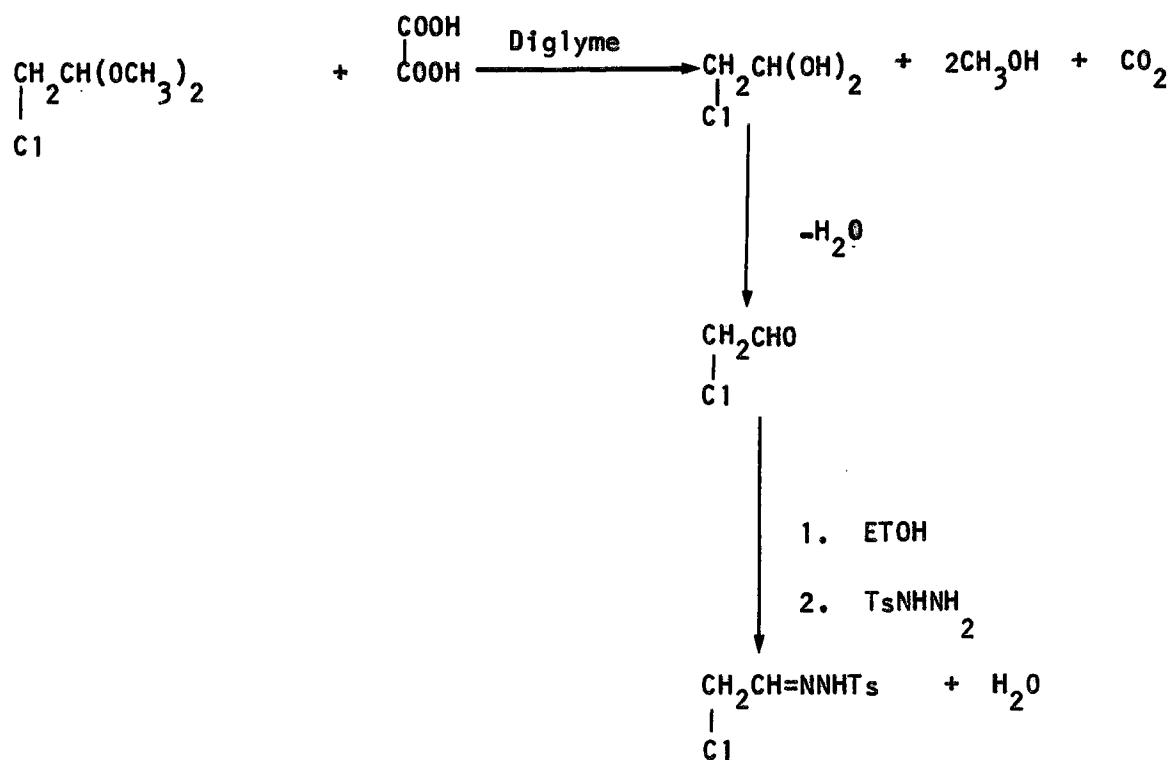
The mechanism to account for the formation of 20 can be described as follows: the p-toluenesulfinate anion formed from the dissociation of 17 so adds to the diazonium cation forming 18. A part of the vinylic diazonium 17 undergoes an internal neutralization leading to the alkyne, 21, nitrogen and a proton. The latter protonates the diazo group 18, and by nitrogen expulsion and later elimination of H⁺, 19 is formed. This species is believed to dimerize to form 20. Alternatively 19 can also be formed via a carbonium mechanism as indicated in pathway 2 leading to the formation of 20. The structure of 20 is a tentative assignment which has been based on spectroscopic and analytical data. Compound 20 is isolated as a white solid, mp 102°. In the nmr spectrum 20 showed resonances at $\delta=.80$ (6H, multiplet), 1.42 (6H, singlet), 1.60

(6H, multiplet), 2.46 (6H, singlet), 7.34 (4H, doublet), 7.72 (4H, p-ArH) ppm. In the ir bands were observed at 3.01 (w), 6.31 (w), 7.68 (s), 7.78 (s) and 9.25 (m) μ . The ir showed no gem dimethyl groups or -NH- stretching frequency.

Extensive mechanistic studies of the mechanism proposed in Scheme III, pathway 1 and 2, have not been carried out and, consequently, the decomposition of the diazonium ion 17 via vinyl carbonium ions is, at present, as likely as the one depicted. The isolation and identification of 16 establishes that cleavage of p-toluenesulfinic acid does occur with expulsion of nitrogen. The 1,4-addition of p-toluenesulfinic acid to undecomposed p-tosylazoenes seems to be a general reaction and can occur in protic as well as aprotic solvents.^{15,16} The first step for the dissociation of 13 indicates a S_N1 mechanism or dissociation into a intimate ion pair. The formation of the other products suggests a carbonium ion mechanism with subsequent rearrangement. This pathway could occur by two different pathways as indicated in Scheme III. However, we know of no precedent for the dimerization of 19 to 20. No evidence for the formation of the alkyne 21 was obtained in our laboratory.

Efforts to further elucidate the mechanism for the decomposition of the azoene 13 have been made. An attempt was made to prepare the tosylhydrazone of chloroacetaldehyde. Chloroacetaldehyde was prepared from the oxidation of chloroacetaldehyde dimethyl acetal in diglyme in 56 percent yield. The resultant tosylhydrazone isolated after removal

of the solvent in vacuo was a yellow viscous liquid that did not crystallize on standing. Under the conditions adopted for the reaction, the isolation of the desired product was unsuccessful since the tosylhydrazone apparently decomposed at the temperature of the reaction. The pathway for the preparation of these compounds is illustrated in Scheme IV.



Scheme IV

We wish to point out in conclusion that this thesis is not meant to be a comprehensive study of all the reactions of tosylazoenes and we have therefore restricted our study to the tosylazoene formed from the α -chloroisobutyraldehyde system. Our principal interests have been directed to structure determination and mechanism for the decomposition of the azoene 13. It remains to explain what effects change in solvent polarity will have on the initial decomposition of the azoene 13. It is therefore suggested that future work include the following: (a) following the course of the decomposition of the azoene in a protic solvent to see if an increase in yield of the 1,4-addition product is obtained and the possible isolation of any unsaturated product that may form, (b) using a system or systems of higher molecular weight in an effort to generate an azoene of greater stability and (c) following the course of the decomposition of the azoene 13 using ultraviolet spectroscopy in order to determine the kinetics of the reaction.

EXPERIMENTAL

Melting points were taken with a Fisher-Johns or Thomas-Hoover melting point apparatus and are uncorrected. Infrared (ir) spectra were recorded with a Beckman Model IR-5A Spectrometer and calibrated against the $6.24\ \mu$ band of a polystyrene film. Unless otherwise stated, spectra were obtained using either chloroform or carbon tetrachloride as a solvent. Only the most prominent bands in the spectra are listed with the following abbreviations: s=strong, m=medium, w=weak, sh=shoulder. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60A high resolution spectrometer with a variable temperature probe. Chemical shifts (δ) are reported in ppm downfield from internal tetramethylsilane. Analytical thin layer chromatography (tlc) was accomplished on 5x20 cm plates coated with MN Silica Gel S-HR UV active. Components were visualized using a UVS-II short wave ultraviolet lamp. Gas liquid partition chromatography (glc) was conducted on an Aerograph Model A-90-P3 or a F and M Model 700. The column used was 6' x $\frac{1}{4}$ " SE 30 unless otherwise stated. Ultraviolet (uv) spectroscopy was accomplished on a Coleman-Hitachi EPS-3T spectrophotometer. All Electron Spin Resonance (esr) spectra were taken by Mr. James Barefield, Morehouse College, on a Varian E-3 Spectrometer. Elemental microanalysis were done by the Atlantic Microlab, Inc., Atlanta, Georgia.

Removal of solvent in vacuo or at rotary evaporator refers to evaporation using an all glass Buchler rotary evaporator.

2-Chloro-2-methylpropanal (11).-- In a 250 ml flask equipped with a dropping funnel, stirrer and reflux condenser protected with a gas absorption trap was placed 36.5 g (0.5 m) of isobutyraldehyde (Eastman). To the aldehyde 40.2 g (0.5 m) of freshly distilled sulfuryl chloride was added slowly with agitation to maintain a temperature of 25-40°. After the addition was completed (ca. 90 min) the reaction was heated for 2 hr and stirred overnight, then flash distilled, bp 85-86°/40mm. Final distillation through a 5 cm Vigreux column at atmospheric pressure yielded 64 g (60%) of α -chloroisobutyraldehyde, bp 88°, n_D^{20} 1.4249 lit.²³ 87°, n_D^{20} 1.4228 ; ir (CCl₄) 5.83 (s), 7.21 (s), 7.31 (s), 8.95 (s), 10.50 (s) and 10.95 (s) μ ; nmr (CCl₄) δ =1.68 (6H, singlet, gem dimethyl), 9.02 (1H, singlet) ppm.

When stored at room temperature or at refrigerator temperature the α -chloroisobutyraldehyde trimerized either in the presence of a trace of acid or during long standing. The resultant trimer melted at 107°. The monomeric haloaldehyde was regenerated from its trimer by distillation and was stored at room temperature under nitrogen.

Preparation of the Halo 2,4-Dinitrophenylhydrazone.-- A 2,4-dinitrophenylhydrazone derivative of the α -chloroisobutyraldehyde (11) was prepared according to the method of Shriner and Fuson²⁴ in 95 percent ethanol. The yellow solid, mp 118° (lit.²⁵ 116°), corresponded to α -ethoxyisobutyraldehyde-2,4-dinitrophenylhydrazone.

2-Methyl-2-chloropropanal-1-p-toluenesulfonylhydrazone (12).--

Para-toluenesulfonylhydrazide, 1.86 g (0.01 m), dissolved in 50 ml of methylene chloride was placed in a 250 ml 3-neck flask fitted with a drying tube. Five gm of anhydrous sodium sulfate was added and the mixture cooled in an ice water bath. To this, 1.01 ml (0.01 m) of α -chloroisobutyraldehyde was slowly added with a syringe. The mixture was allowed to stir for 1½ hr, filtered and the solvent removed in vacuo yielding a white solid, mp 86° (100%). Attempts to further purify the product through recrystallization resulted in decomposition. The ir showed no C=O stretching mode, but showed peaks at 2.95-3.05 (w), 6.85 (m), 7.21 (m), 7.31 (m) μ ; nmr (CDCl₃) δ =1.76 (6H, singlet, gem dimethyl), 2.50 (3H, p-ArCH₃), 5.41 (1H, vinyl -CH=), 7.42 (2H, doublet, p-ArH), 7.86 (3H, doublet, p-ArH and -NH-) ppm.

1-p-Toluenesulfonylazo-2-methylpropene (13).--Compound 12, 1.15 g

(4.4 mm), was dissolved in 20 ml of anhydrous ether and was placed in a 3-neck flask that was previously flushed out with nitrogen. While keeping the nitrogen atmosphere constant, 10 ml of a saturated sodium bicarbonate solution was added and the solution allowed to stir for 40-60 min. The ether layer was separated, dried over anhydrous magnesium sulfate, filtered and the solvent removed in vacuo yielding a bright yellow solid in quantitative yield. Spectral analysis (nmr) at -10° showed signals at δ =2.16 (6H, singlet, gem dimethyl), 2.52 (3H, singlet, p-ArCH₃), 7.06 (1H, singlet >C=CH-), 7.46 (2H, doublet, p-ArH, J=8 Hz) and 7.74 (2H doublet, p-ArH, J=8 Hz) ppm; uv (cyclohexane) 227 m μ _{max}

(ϵ 6800), 277 m μ (ϵ 14,545) and 420 m μ (ϵ 10). The compound decomposed within minutes at room temperature but is fairly stable for days at 0°.

Decomposition of 1-p-Toluenesulfonylazo-2-methy-propene-2 in Chloroform.-- Compound 13, 3.62 g (0.16 mm), dissolved in a minimum amount of chloroform was placed in a flask connected to a gas buret. The yellow solution was allowed to stir at room temperature until the yellow color of the solution disappeared (ca. 4 hr). Thin layer chromatography showed that the solution contained a variety of products. The solution was concentrated in vacuo and taken up in a minimum amount of pentane and chromatographed on neutral alumina. Elution with 20% benzene-pentane solution afforded 16, mp 132° (13%) as one of the pre-pondant products. The amount of gas evolved, measured at room temperature, corresponded to a yield of 50% (48.9 ml) of the available gas. The purity of the solid was checked by tlc and glc using a carbowax column at 125°. The nmr spectrum (CDCl₃) showed signals at δ =1.36 (6H, singlet, gem dimethyl), 2.41 (6H, singlet, p-ArCH₃), 7.2 (9H, multiplet, p-ArH and >CH=) ppm; ir (CHCl₃) 2.95 (w), 6.3 (m), 7.22 (m), 7.32 (m) μ .

Anal. Calcd. for C₁₈H₂₂N₂O₄S₂: C, 54.80; H, 5.62; N, 7.11; O, 16.23; S, 16.25. Found: C, 54.67; H, 5.76; N, 7.06; O, 16.30; S, 16.21.

Spectroscopic results and microanalytical data led to the assignment of this compound as 2-methyl-2-tosylpropanal-1-p-toluenesulfonyl-hydrazone (16). When 13 is allowed to stir in a minimum amount of carbon tetrachloride, product 16 separates as a solid which can be

further purified by chromatography. The yield in both cases is about the same.

Further elution of the column with a 30% benzene-pentane solution yielded another white solid, mp 102° (49.4%), with different nmr shift and absorption intensity. The nmr spectrum (CDCl_3) showed signals at $\delta = .80$ (2H, multiplet), 1.42 (6H, singlet), 1.60 (6H, multiplet), 2.46 (6H, singlet), 7.34 (4H, doublet, \underline{p} -ArH, $J=9$ Hz), 7.72 (4H, \underline{p} -ArH, $J=9$ Hz) ppm. There was no vinyl hydrogen splitting pattern in the nmr spectrum and the compound gave a negative test for unsaturation. In the ir there was no -NH- stretching mode but bands were observed at 3.01 (w), 6.31 (w), 6.55 (w), 7.68 (s), 7.78 (s) and 9.25 (m) μ .

Anal. Calcd. for $\text{C}_{22}\text{H}_{28}\text{O}_4\text{S}_2$: C, 62.82; H, 6.71; S, 15.25; O, 15.22. Found: C, 62.62; H, 6.62; S, 15.01; O, 15.75.

Spectroscopic results and microanalysis suggested the tentative structure for this compound as 1,2-di- \underline{p} -tosyl-1,2,3,4-tetramethylcyclobutane (20) which could be formed from the dimerization of 2- \underline{p} -tosylbutene-2.

Preparation of Chloroacetaldehyde.-- Chloroacetaldehyde dimethyl acetal, 12.6 g (1 m), dissolved in 25 ml of diglyme was added to 12.6 g (1 m) of oxalic acid. The mixture was refluxed for $2\frac{1}{2}$ hr and distilled at atmospheric pressure to yield 7.7 g (61.6%) of a product which showed ir bands at 2.9-3.1 (s, broad), 5.82 (s), 6.2 (m) and a broad band between 9.3-9.6 μ . Redistillation of the semihydrate, bp 84° (lit²⁵ bp 86°), yielded 5.7 g (56%) of chloroacetaldehyde; ir (CCl_4) 3.42 (s), 3.56 (s), 5.79 (s), 6.95 (s), 7.01 (s), 8.5 (m), 12.3

(s) and 13.15 (s) μ ; nmr (CCl_4) δ =3.62 (2H, doublet, J =5 Hz) and 9.58 (1H, triplet) ppm.

Reaction of Chloroacetaldehyde with p-Toluenesulfonylhydrazide.--

Chloroacetaldehyde, 2.3 g (.02 m), dissolved in 20 ml of 95% ethanol was added to 1.86 g (.01 m) of p-toluenesulfonylhydrazide. The solution was allowed to stir at room temperature for 1 hr. The colorless solution changed to a pale yellow, then darkened within a few minutes. Evaporation of the solvent in vacuo yielded a very viscous liquid that did not crystallize on standing. Spectral analysis (nmr) showed a complicated pattern for the methylene protons which was unlike that of the desired product. The reaction was repeated but isolation of the pure p-tosylhydrazone was unsuccessful.

Reaction of 1-p-Toluenesulfonyl-2-methylpropene with Sodium

Hydride.-- The p-tosylazoene 13, 1.37 g (5 mm), was dissolved in 20 ml of dry chloroform and placed in a 100 ml 3-neck flask to which a gas delivery tube was connected. The gas delivery tube was then channeled into a 2% bromine-carbon tetrachloride solution. The solution was allowed to stir for 2 hr at room temperature. The residue was washed consecutively with three 15-ml portions of water, dried over anhydrous sodium sulfate, and the solvent removed through distillation. In the ir, the residue showed bands at 2.92 (w), 3.42 (s), 3.61 (s), 5.83 (s), 7.21 (m) and 7.31 (m) μ .

The bromine-carbon tetrachloride solution was disconnected from the flask and concentrated in vacuo. No signals were observed when the

residue was scanned on the nmr.

Decomposition of 1-p-Toluenesulfonylazo-2-methylpropene in Potassium tertiary-Butoxide.-- The tosylazoene 13, 1.37 g (5 mm), was placed in a 3-neck flask fitted with a nitrogen gas delivery tube and cooled in a Dry ice-acetone bath. While keeping the nitrogen atmosphere constant, 25 ml of cyclohexene was added. An excess of potassium tertiary-butoxide was added and the solution allowed to stir for 2 hr at -78° and finally for 2 hr at room temperature. The solution was washed consecutively with three-15 ml portions of water, dried over anhydrous magnesium sulfate and concentrated in vacuo. Analysis of the residue by glc (column temperature 125°) showed a major peak at the approximate retention time of cyclohexene and a minor peak attributed to impurity in the cyclohexene. No peaks were observed for the cyclohexene adduct of 2-methylvinylidene 15.

Another sample was prepared and the same conditions were followed as above, except for the following: after stirring at -78° for 2 hr the solution was warmed to room temperature and finally refluxed for 2 hr at 120° . Follow-up procedures were the same. Analysis by glc showed no peaks at the approximate retention time of the cyclohexene-2-methylvinylidene adduct.

Thermal Decomposition of 1-p-Toluenesulfonylazo-2-methylpropene in Carbon Tetrachloride.-- The tosylazoene 13, 1.37 g (5 mm), was dissolved in 25 ml of carbon tetrachloride and heated for 30 min. The solvent was then distilled into a Dry ice-acetone cooled flask and scanned on the nmr. No peaks were observed for any unsaturated products.

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